SEPARATION AND CHARACTERIZATION OF LIGNITE DERIVED PREASPHALTENES BY GEL PERMEATION CHROMATOGRAPHY AND NUCLEAR MAGNETIC RESONANCE SPECTROMETRY

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INTRODUCTION

Methods for the separation and chemical characterization of the preasphaltene components in lignite liquefaction products has been understudied by our group for several years. Preasphaltenes for purposes of this study are defined as that portion of a lignite derived product which is soluble in tetrahydrofuran but insoluble in toluene. The preasphaltenes studied would fall into the seventh and eighth fractions of the sequential elution by solvent chromatography (SESC) procedure developed by Farcasiu (1). Further elution chromatography of the tetrahydrofuran preasphaltene fraction on silica or alumnia did not appear to be justified in view of the highly polar nature of the fractions. The preasphaltene fraction was chromatographed for size separation using Bio-Beads S-X3 columns and pyridine as the eluent (2). The distribution and functionality of nitrogen and oxygen were then monitored in the molecular size fractions formed at different operating conditions. The study shows the structure and distribution of oxygen is the most important parameter. Work of our group has centered on the development of procedures of the quantitation of oxygen functionality in this material. For this report we are only able to identify the amount of phenolic hydroxyl groups present. Work is continuing on the development of a number of quantitative ether cleavage reactions (3).

EXPERIMENTAL

Materials.

Solvent refined lignite (SRL) was produced at 404°, 460° and 480°C, 26.2 MPa (3850 psi) from Beulah 3 North Dakota Lignite. The reducing gas used was a 1:1 mol mixture of carbon monoxide and hydrogen. The SRL was produced in a 5-lb coal/hr continuous process unit at the Grand Forks Energy Technology Center (GFETC) using anthracene oil and 7% wt tetralin as the donor solvent in single pass tests in a continuous-stirred tank reactor (4). The preasphaltene fraction was recovered from the toluene insoluble portion of an SRL using tetrahydrofuran as the solvent in a Soxhlet extractor. Tetrahydrofuran was chosen to define the solubility of preasphaltenes in place of pyridine so that the results could be correlated with data obtained during the liquefaction runs at GFETC (4). Standard compounds used to calibrate the GPC and to acetylate the SRL were obtained from commercial sources.

Preparative Scale GPC.

Preparative scale GPC separations were carried out with a 22 mm i.d. X 1 m glass column packed with Bio-Rad, SX-3, Bio-Beads (200-400 mesh, 3% cross linked, styrene-divinyl benzene). The preasphaltene was acetylated by reaction with acetic anhydride in pyridine for 24 hr at 25°C. We found the total preasphaltene sample to be soluble in chloroform. Upon attempting to use this solvent with 1g of sample we found that some precipitation occured on the GPC column during separation. The elution solvent was changed to pyridine. About one gram of sample dissolved in 5 ml of solvent was charged to the column. A flow rate of 1.5 ml/min was maintained by a constant head devise. Fractions were collected every 5 ml which were then stripped of solvent in a rotary evaporator, added to 3-5 ml of benzene and free dried to remove the last traces of pyridine. The last traces of benzene were removed by drying in an abderhalden apparatus at 80°C under vacuum.

Analyses.

Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI. Molecular weights were determined at our laboratory with a Wescan Vapor Pressure Osmometer. Molecular weights were measured over a range of 0.1 to 4 g/kg using the solvent pyridine. Several fractions were run at three different concentrations for extrapolation to infinite dilution. No evidence for intermolecular association in pyridine was noted so single point analyses were measured because of the large number of fractions to be analyzed.

Proton NMR spectra were obtained on a Varian EM-390 Spectrometer. Samples were dissolved in d_5-pyridine containing a known amount of s-trioxane as an internal standard. Correction for residual pyridine protons was based on the standard versus residual pyridine integration. Generally, seven integrations were run and averaged. The data was analyzed using modified Brown-Ladner equations (5).

All samples of preasphaltenes were acetylated with 1-^{14}C acetic anhydride in pyridine under argon. The samples of acetylated SRL were weighed in combustocones (Packard Instrument CO, Downers Grove, ILL.) and then oxidized in a Packard Model 306 automatic sample oxidizer for subsequent liquid scintillation measurement. The counting was carried out in a Packard model 3375 liquid scintillation spectrometer. When SRL was allowed to react at room temperature for 24 hr only the hydroxyl and amine sites are derivatized. If the acetylation is carried out a reflux temperature (115°C) some aromatic carbon acetylation results (6).

RESULTS AND DISCUSSION

Molecular Weight Distribution

Seven to eight fractions each of five ml were collected for each GPC run. The fraction of total weight recovered from the original weight of material is reported in Table 1. Two solvent refined coal preasphaltene samples are added to the table from comparison with the lignite derived

material. The average molecular weight distribution goes to higher molecular weights with increased reaction temperature for the lignite preasphaltenes. The coal derived preasphaltenes have much higher molecular weights. The lignite preasphaltenes were 38, 25 and 21% wt, maf of the 400°, 460°, and 480°C lignite derived products. The molecular weight increase for the 480°C material is an indication the extent of recombination that occurs at the high temperature. The fact that the 400°C material has similar $\bar{M}n$ values as the 460°C may occur because higher molecular weight portions may lie in the tetrahydrofuran insoluble portion which is 35% wt of the original lignite at 400°C as compared to 15% wt at 460°C.

Nitrogen and Sulfur Distribution

Table 1 shows that the distribution of nitrogen and sulfur is spread evenly throughout the fractions. The distribution of nitrogen and sulfur is only slightly reduced with increased temperature for the lignite preasphaltene samples. Both of the above facts would be consistent with the nitrogen and sulfur being present in ring systems such as carbazoles, pyridines, and thiophenes. Nonaqueous titration data shows that approximately 50% of the nitrogen is present as basic nitrogen (7).

Oxygen Distribution

The hydroxyl contents were determined by carbon-14 counting of the labeled acetate added by the acetylation process. Earlier work has shown that there are few alcoholic hydroxyl or amine sites present in these type of samples (6). Carbazole acidic hydrogen does not react under the acetylation conditions used (6). Greater than 95% of the added acetate is due to phenolic hydroxyl sites and for purposes of this study was assumed 100%. The total oxygen content of each fraction was determined by difference with the carbon, hydrogen, nitrogen and sulfur analyses. In the past we have checked the validity of this assumption by comparison of neutron activation analysis data with this procedure and found the agreement was within ± 5% relative error (7).

Table 2 and 3 show the distribution of total oxygen, phenolic oxygen and other oxygen reported in millimoles per gram or per mole of sample. Insight is gained about the structure by comparison of the concentration of oxygen in several ways. The total oxygen content expressed in millimoles per gram is nearly constant with molecular weight for a given liquefaction temperature. There is a small increase in total oxygen millimoles per gram with decreasing molecular weight but this explained by the an increase in phenolic oxygen per gram as the molecular weight decreases. The millimoles of phenol per mole of lignite preasphaltene is near 1 phenolic site per average molecule. The constant concentration of other oxygen per gram at constant temperature could be due to a repeating structure of aromatic centers connected by ether or furan linkages as shown in the hypothetical models in figures 1-2. For the lignite preasphaltenes one finds there are 8-9, 20-23 and 16-23 aromatic carbon molecules per other oxygen mole, for 404, 460, and 480°C respectively, as shown in table 2. This is reflected in the structures drawn on figure 1 where benzene rings predominent for the 404°C material. As the reaction temperature is raised the aromatic centers begin to show more and more condensation as in figure 2.

Carbon Structure

Table 4 shows the values of f_a, the fraction of aromatic carbons, and D, the degree of condensation, calculated from modified Brown-Ladner equations:

$$f_a = \frac{C/H - (H\alpha^*/2 + Ho^*/2 + OH/2H)}{(C/H - 2OH/H)} \quad (1)$$

The term was OH/H is included in equation 1 to remove the carbonyl carbon present because of the acetylation.

$$D = \frac{H^*_{ar} + H^*_{\alpha}/2 + n[OH/H] + OH/H}{fa(C/H - 2OH/H)} \quad (2)$$

Equation 2 assumes that all the other oxygen is present in the polymeric molecules as connecting furan linkages (n=4) or ether linkages (n=2). This has not been proven in this study. The development of a furan or ether analysis technique is a major objective in our studies and we add the ether linkages only to show the importance of oxygen to the preasphaltene structure. Figures 1-2 show the furan and ether linkages with the corresponding values of f_a and D as counted from the hypothetical average molecule and from equations 1 and 2 using the NMR data. The calculated values are in good agreement with the model. The true value of D depends upon the correct assignment of n through a quantitative ether analysis.

Comparison to Asphaltene

Table 5 shows the oxygen distribution for a series of asphaltene samples. The main difference between the preasphaltenes and the asphaltenes is other oxygen concentration. The phenol concentrations, molecular weights, and f_a are approximately equal.

Conclusions

Gel permeation chromatography offers the opportunity to observe subtle changes in preasphaltene structure that would be rather difficult to observe by another procedure. The postulated aromatic core plus ether links polymer structure requires precise information about the concentration of phenolic sites as they change with molecular weight. The type of preasphaltene structure suggested by this study would explain why preasphaltenes are insoluble in benzene even through their acidities, basicities and fraction of aromatic carbons may be equal to those of asphaltenes. Their insolubilities results from ether and furan linkages locking the aromatic systems into very rigid condensed molecules.

ACKNOWLEDGMENT

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LITERATURE CITED

1. Farcasiu, M., Fuel, 56, 9 (1977).

2. Coleman, W.M., Wooton, D.L., Dorn, H.C., Taylor, L.T., J. of Chrom., 123, 419 (1976).

3. Baltisberger, R.J., Woolsey, N.F., Stenberg, V.I. and Klabunde, K.J., Quarterly Rpt, Conversion of Solvent Refined Lignite into Premium Fuels, FE-2211, April-June, 1980.

4. Wilson, W.G., Knudson, C.L., Baker, G.C., Owens, T.C. and Severson, D.E., Application of Liquefaction Process to Low-Rank Coals, 1979 Symposium on Technology and Use of Lignite, Grand Forks, ND, May, 1979.

5. Brown, J.K. and Ladner, W.R., Fuel, 39, 87 (1960).

6. Baltisberger, R.J., Klabunde, K.J., Woolsey, N.F. and Stenberg, V.I., Final Rpt, Chemistry of Lignite Liquefaction, FE-2211, August, 1980; Submitted to Fuel for publication.

7. Baltisberger, R.J., Klabunde, K.J., Stenberg, V.I., Woolsey, N.F., Saito, K. and Sukalski, W., ACS Symposium Series No. 71, Organic Chemistry of Coal, J.W. Larsen Ed. pp 294-300, 1978.

Table 1. Distribution of Nitrogen and Sulfur

Preasphaltene Samples

Sample	$\%_{wt}$,N	$\%_{wt}$,S	$M\bar{n}$	Wt, %[a]
Y-15-2	1.48	0.52	582	0.15
(400°C)	1.30	0.57	573	0.26
	0.89	0.48	373	0.17
	0.85	0.47	218	0.07
	0.86	0.45	219	0.07
	0.89	0.52	224	0.07
26-Y-7	1.90	0.51	568	0.09
(460°C)	1.63	0.75	626	0.23
	1.37	0.54	429	0.20
	1.24	0.67	302	0.14
	1.14	0.49	240	0.08
	1.05	0.59	240	0.07
26-Y-11	1.43	0.46	1165	0.22
(480°C)	1.26	0.47	831	0.31
	1.27	0.46	607	0.22
	1.22	0.64	463	0.09
Beulah 3 Lignite	.80	3.03	---	---
Tacoma[b]	2.63	---	2400	0.08
	2.32	---	1600	0.24
	2.07	---	1450	0.22
	1.95	---	800	0.17
	2.15	---	800	0.12
	1.96	---	655	0.08
Indiana[c]	2.22	---	2300	0.10
	1.97	---	1600	0.22
	2.11	---	1300	0.21
	1.85	---	830	0.17
	1.76	---	810	0.12
	1.88	---	560	0.07

[a] wt% of recovered starting material

[b] prepared at 450°C, 10MPa H_2, recycle solvent

[c] prepared at 441°C, 12MPa H_2, recycle solvent

Table 2. DISTRIBUTION OF ETHERAL AND ACID OXYGEN IN GFETC PREASPHALTENE SAMPLES

Sample	Mole wt gm/mole	Total O_2 mmol/gm	OH mmol/gm	OH mol/mol	Etheral O_2 mmol/gm	Etheral O_2 mol/mol
15-Y-2	582	8.9	1.8	1.0	5.3	3.1
(400°C, 26MPa)	573	9.1	1.9	1.1	5.3	3.0
	373	9.7	2.4	0.9	4.9	1.8
	218	10.6	2.7	0.6	5.2	1.1
	219	10.8	2.9	0.6	5.0	1.1
	224	10.6	2.9	0.6	4.8	1.1
26-Y-7	568	6.5	1.4	0.8	3.7	2.1
(460°C, 26MPa)	626	5.8	1.5	0.8	2.8	1.8
	429	7.0	1.7	0.7	3.6	1.5
	302	7.6	2.3	0.7	3.0	0.9
	240	8.2	3.0	0.7	2.2	0.5
	240	8.8	3.3	0.8	2.2	0.5
26-Y-11	1165	5.6	1.0	1.2	3.6	4.2
(480°C, 26MPa)	831	5.7	1.4	1.2	2.9	2.4
	607	5.9	1.5	0.9	2.9	1.8
	463	6.5	1.9	0.9	2.7	1.3

Lignite, Beulah 3 - 19.57% O_2 (MAF); 10.6 meq/gm $\approx$ 15% O_2

Table 3. Distribution of Ethenal and Acid Oxygen in SRC Samples

Sample	$\bar{M}n$	Total O_2 mmol/gm	Phenolic OH mmol/gm	Phenolic OH mol/mol	Etheral O_2 mmol/gm	Etheral O_2 mol/mol
Tacoma	2400	5.4	1.3	3.1	2.8	6.7
	1600	5.6	1.4	2.2	2.8	4.5
	1450	5.8	1.5	2.2	2.8	4.1
	800	5.9	1.5	1.2	2.9	2.3
	800	5.3	1.6	1.3	2.1	1.7
	655	4.6	1.65	1.1	1.3	0.9
Indiana	2300	6.5	1.5	3.5	3.5	8.05
	1600	7.2	1.65	2.6	3.9	6.2
	1300	6.0	1.8	2.3	2.4	3.1
	830	6.5	1.9	1.6	2.7	2.2
	810	6.1	2.0	1.6	2.1	1.7
	560	6.4	2.0	1.1	2.4	1.3

Table 4. Structural Features of GFETC Preasphaltenes

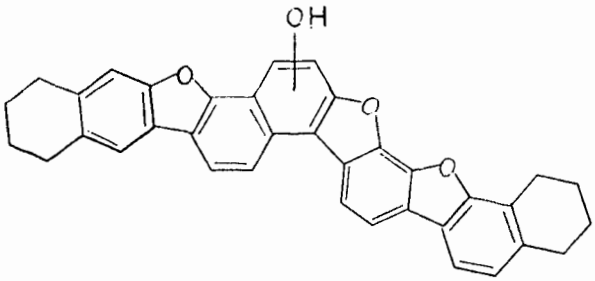
Sample	$\bar{M}n$	f_a	D (n = 2)	D (n = 4)	C_T
15-Y-2	582	0.735	0.94	1.02	2.0
	573	0.76	0.91	0.99	2.1
	373	0.75	0.91	1.01	1.8
	218	0.73	1.02	1.14	1.6
	219	0.69	1.01	1.27	1.6
	224	0.68	1.07	1.32	1.6
26-Y-7	568	0.84	0.72	0.85	1.8
	626	0.83	0.65	0.75	1.8
	429	0.84	0.73	0.86	1.8
	302	0.795	0.80	0.92	1.4
	240	0.76	0.84	0.94	1.4
	240	0.74	0.94	1.05	1.4
26-Y-11	1165	0.86	0.68	0.80	1.6
	831	0.84	0.69	0.79	1.5
	607	0.84	0.71	0.81	1.4
	463	0.83	0.73	0.83	1.4

Table 5. Asphaltene

Sample	$\bar{M}n$	O, mmol/gm	OH, mmol/gm	Ref	Etheral O_2 mmol/gm
Asphaltene 1	615	2.2	---	a	---
Asphaltene 2	860	2.6	---	a	---
Asphaltene 3	415	2.5	---	a	---
Synthoil	---	2.4	1.8	b	0.6
FMC-COED	---	4.4	3.6	b	0.8
SRC, Catalytic	---	2.9	2.25	b	0.65

[a] B.C. Bockrath, Anal Chem, 51, 1168 (1979).

[b] T.F. Yen, Anal Chem, 51, 569 (1979).



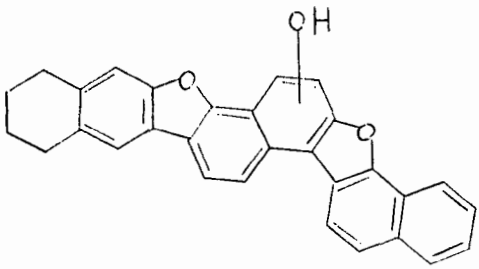
$C_{35.2}H_{25.8}(OH)_1O_{3.2}N_{0.6}S_{0.1}$

$f_a = 0.77$; 0.74(NMR)

D = 0.93 ; 1.02(NMR, n=4) , 0.94(NMR, n=2)

$C_1 = 2.0$; 2.0

Figure 1. Fraction one, 404°C



$C_{28}H_{17.8}(OH)_{0.7}O_{1.7}N_{0.4}S_{0.07}$

$f_a = 0.86$; 0.84(NMR)

D = 0.85 ; 0.86(NMR, n=4), 0.73(NMR, n=2)

$C_1 = 2.0$; 1.8

Figure 2. Fraction three, 460°C